

**CONDUCTING POLYMER FOR PRETREATMENT
OF METALLIC AND NON-METALLIC SURFACES**

PRIORITY INFORMATION

5 This application claims priority to U.S. Provisional Patent Application No. 60/325,419, filed September 27, 2001, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

10 This invention is directed to the synthesis of double-stranded conducting polymers, formulation for surface treatment reagents, and the use of water-borne double-stranded conducting polymers.

15 In the treatment of metal surfaces to prepare the surface for the application of a primer or other coating, chromate based metal finishing compositions have been the industry standard. The chromate-based metal finishes serves two functions, corrosion inhibition and adhesion enhancement. The chromates are toxic and environmentally unfriendly. Thus, the EPA and OSHA are tightening the usage of chromate-based metal finishing technology. The existing chromate-based metal finishing technology will be banned from use because of the toxicity of the hexavalent chromate. Therefore, the metal finishing industry is seeking an alternative to chromate-based surface treatments. Currently, the industry is shifting to non-chromate 20 phosphate-based metal finishes. One problem with phosphate-based metal finishes is that they lack corrosion resistance.

Currently, there are no coatings that can be used for reporting the early stage of corrosion

SUMMARY OF THE INVENTION

This invention concerns the synthesis of double-stranded conducting polymers, a formulation for surface treatment reagents, and the use of water-borne double-stranded 5 conducting polymers for the following types of applications: a surface conversion or surface treatment agent for metal surfaces; an early-warning indicator for metal corrosion; a component for a wash primer for aluminum alloys, magnesium alloys, steel and other non-noble metals; a surface modification coating on non-metallic surfaces to catalyze deposition of decorative and functional top coatings; an additive to improve the performance of adhesive bonding of metals; 10 and for others that are logical extensions of the above application.

The invention involves the integration of the appropriate ligands in the second strand. A carboxylic function group helps binding the polarized metal atoms on the surface. A phosphate functional group helps binding with the metal oxides and the formation of crystalline nano-composite with the microcrystals nucleated on the metal surface. Adhesion or miscibility with 15 an organic surface, is provided by attaching hydrophobic organic functional groups on the second strand provide. The organic polymer, metal phosphate, metal oxide and metal, forms a composite material at the interface. This interface is mechanically sturdy, chemically stable and it serves as a regeneratable self-healing interface.

The invention involves the use of conducting polymers of the invention as a component 20 (additive) in the currently existing formulation, without the chromates and phosphates. The use of water-borne conducting polymer will provide metal finishing that will provide the dual function of corrosion resistance and adhesion enhancement.

The compositions can be used to treat metal surfaces to provide a stable interface for

adhesive binding or the coating of paint or plastics on top of the chemically modified surface. This composition is useful as a replacement of chromate-based surface treatment process.

There are many advantages of the conducting polymers of the present invention including the new metal finishing (surface treatment) technology include no toxic chromates, enhances the 5 performance of phosphate treatment and water-base, and there is no emission of volatile organic compounds (VOC). In the area of heavy metal removal from solutions, they are effective and convenient. An additional advantage of the new process is to be able to reclaim the precious metals efficiently and cheaply.

An object of the present invention is to provide a double-stranded conducting polymer. 10 Another object of the invention is to provide formulation for surface treating reagents.

Still another object of the invention is to provide double-stranded conducting polymers to use as a surface conversion or surface treatment agent for metal surfaces; as an early-warning indicator for metal corrosion; as a component for a wash primer for aluminum alloys, magnesium alloys, steel and other non-noble metals; as a surface modification coating on non-15 metallic surfaces to catalyze deposition of decorative and functional top coatings; as an additive to improve the performance of adhesive bonding of metals; and for others that are logical extensions of the above application.

These and other objects, features and advantages of the present invention will become apparent in light of the following detailed description of preferred embodiments thereof, as 20 illustrated in the accompanying drawings.

DETAILED DESCRIPTION OF THE INVENTION

The double-stranded conducting polymer provides a unique flexibility in designing molecules for surface treatment. The first strand of the polymeric complex has the property of being a reversible electron donor or acceptor. This reversible charge-transfer interaction with a metallic surface is not available for the existing state-of-the-art chemicals for surface treatment. The second strand of the complex can be designed to carry the properties of the normal surface treatment agents and, in addition, a synergistic interaction with surface atoms in a cooperative interaction with the first strand.

10 The second strand includes the integration of appropriate ligands. A carboxylic function group helps binding the polarized metal atoms on the surface. A phosphate functional group assists with binding the metal oxides and the formation of crystalline nano-composite with the microcrystals nucleated on the metal surface. Attaching hydrophobic organic functional groups on the second strand provides adhesion or miscibility with organic surface. The organic 15 polymer, metal phosphate, metal oxide and metal form a composite material at the interface. This interface is mechanically sturdy, chemically stable and it serves as a regeneratable self-healing interface.

An example of the molecular design of synergistic interaction is to use the first strand to accept electrons from the surface states of the metal atoms, thus polarizing the surface atoms to 20 promote chemical bonding (ligand-to-metal bond) between the metal surface and the second strand of the polymer. This type of dual functionality is not available in the conventional organic or inorganic surface treatment. The present state-of-the-art surface treatment chemicals do not have the capability of integrating two functions in one single molecule. In many situations, the

performance cannot be achieved by a physical mixture of the two types of molecules. Thus, the focus is on the applications that require the synergistic interactions to be located within the same molecule. The double-strand synthetic polymer is a very good way to achieve the “bias-and-react” type of surface binding.

5 The design concept involves the integration of the appropriate ligands in the second strand. A carboxylic function group helps binding the polarized metal atoms on the surface. A phosphate functional group helps binding with the metal oxides and the formation of crystalline nano-composite with the microcrystals nucleated on the metal surface. Attaching hydrophobic organic functional groups on the second strand provide adhesion or miscibility with organic 10 surface. The organic polymer, metal phosphate, metal oxide and metal form a composite material at the interface. This interface is mechanically sturdy, chemically stable and it serves as a regeneratable self-healing interface.

The new compositions can be used to treat metal surfaces to provide a stable interface for adhesive binding or the coating of paint or plastics on top of the chemically modified surface. 15 This composition is useful as a replacement of chromate-based surface treatment process.

The new composition can also be used to treat non-metal surfaces, such as plastics, ceramics, fabrics, and glass. The modified surface has an affinity for metal atom deposition. This new interface is then useful for metal plating, metallization of electronic circuit board, etc.

When the new composition is coated on fabrics, the surface of the fabric promotes the 20 formation of precious metal from the waste solutions containing silver and gold. This again involves the synergistic interactions provided by the double-stranded molecular design. The ligand on the second strand promotes the nucleation of metal on the surface of the fabric and thus

the growth of metallic crystals on the fabric. Similar arrangement could be used for removal of mercury from waste water.

Further, the family of water-borne conducting polymers of the invention can be used as a component in metal surface conversion and metal surface treatment formulations to prolong the 5 service life of metal parts in aircraft, machinery, bridges, buildings and appliances.

The conductive polymer film in contact with metals can function as an indicator for the changes of metal surface that precedes a damaging corrosion of metal. Advanced early warning for metal corrosion will lead to increased safety of aircraft, machinery, bridges and buildings and will reduce the maintenance costs.

10 The wash primers of the invention can be used as a non-chromate surface pretreatment solution.

The conductive polymer wash primer is a candidate for replacing the currently used chromate-containing wash primer for metal surface treatment.

15 The new composition can also be used to treat non-metal surfaces, such as plastics, ceramics, fabrics, and glass. The modified surface has an affinity for metal atom deposition. This new interface is then useful for metal plating, metallization of electronic circuit board, etc.

As previously discussed, the invention includes double-stranded conducting polymers. Examples of the double stranded polymer include:

20 Polyaniline:Poly(vinylphosphate) double-stranded complex, Polyaniline:Poly(acrylic acid-co-vinylphosphate) complex, Polyaniline:Poly(methacrylic acid-co-vinylphosphate) complex, Polypyrrole:Poly(vinylphosphate) double-stranded complex, Polypyrrole:Poly(acrylic acid-co-vinylphosphate) complex, Polypyrrole:Poly(vinylmethacrylic acid-co-vinylphosphate) complex, Polyaniline:Poly(methylacrylate-co-vinylphosphate) complex,

Polypyrrole:Poly(methylacrylate-co-vinylphosphate) complex, Polyaniline:Poly(butylacrylate-co-vinylphosphate) complex, and Polypyrrole:Poly(butylacrylate-co-vinylphosphate) complex.

The invention also involves formulations for surface treatment. The compositions of the formulation may include: A water-borne conducting polymer in aqueous or organic solutions (in one embodiment the water-borne conducting polymer is present in the formulation in an amount of 1%), phosphates (dihydrogenammoniumphosphate), an accelerator (e.g., hydrogen peroxide), a surfactant (triton X) for surface wetting, and surface etching and cleaning agent (e.g. phosphoric acid).

An alternative illustrative formulation may contain double-stranded conducting polymer in isopropyl alcohol solutions, such as 1,4-butyldiol in isopropyl alcohol solution and epoxy. Another example of a formulation includes double-stranded conducting polymer in isocyanate and epoxy. Still another example contains: A water-borne conducting polymer in aqueous solution, Polyvinyl-butyral resin dissolved in isopropyl alcohol, butyl alcohol and water; Molybdenum oxide, or cerium oxide, or titanium dioxide, or zirconium hydrogen phosphate, Magnesium silicate and Phosphoric acid.

The compositions can also be used for waste water treatment and precious metal reclamation.

The purpose of metal finish is to temporarily protect the metal from corrosion or rust before a primer coating is applied, and to provide adhesion between the metal and the primer coatings. The conducting polymer will enhance the performance of the existing metal finish processes.

Applications of the composition further include: plating of metal on plastic, wood or ceramic surfaces; nickel, silver or gold plating on electronic circuit board of electronic components; and improving the metal coating of via holes for electronic circuit boards.

The electronic and jewelry industries need to coat metal films onto plastic or ceramic surfaces. Thin conducting polymer coating on nonmetallic surfaces enables the electrode or electrodeless coating of metals from an aqueous solution of metal ions. The conducting polymer helps to accelerate the metal deposition and to improve the adhesion of metal to plastic or ceramics.

Thin conducting polymer coated fibers are efficient for removal of noble metal ions from aqueous solutions. These fibers can be used to reclaim gold, silver and copper from wastes generated by jewelry industry, photographic processing industry and electronic industry. It might also be useful for removing environmentally harmful metal ions such as mercury or radioactive wastes.

Advantages of conducting polymer-based plating of metal on nonmetallic surfaces, includes good quality of via (through-hole) plating, inexpensive method for electrolytic or electrodeless plating.

The conducting polymer-based surface modification for nonmetal can perform better than the existing electrodeless metal coating technology. It can make the coating more uniform and less expensive.

Present technology for metal coating on nonmetallic surfaces involve the use of inorganic catalysts, whereas the invention uses conducting polymers as a surface activation agent. While, present technology for precious metal (e.g., silver) reclamation involves the use of ion exchange resins to adsorb the metal ions. The saturated resin is then chemically reduced a thigh

temperature. The new conducting polymer-based technology integrates the two steps into a single step.

Examples

5 1. Wash primer containing electroactive polymer as a substitute for chromates.

This invention includes a wash primer formulation containing two parts that are mixed immediately before the application of the formulation to steel, aluminum and/or other metal surfaces. The function of the wash primer is to inhibit corrosion of the metal and to enhance 10 adhesion between the metal and the primer or topcoats.

A range of compositions as listed below, can be used as a liquid formulation suitable for spraying, brush painting, or immersion coating of the wash primer on metal. After drying, the alcoholic and water component of the formulation will be evaporated while the remaining coating is in the form of a thin film, adherent to the metal surface. The range of applicable 15 weight percent of the components is listed after the name of the compound.

Part I of the wash primer composition:

20	Polyaniline or polypyrrole	0.5 % to 10 %
	Poly(vinyl butyral)	5% to 30%
	Molybdenum oxide or cerium oxide	0% to 8%
	Magnesium silicate	0% to 2%
25	Carbon black or lamp black	0% to 0.2%
	n-butyl alcohol	2% to 25%
	isopropyl alcohol	40% to 60%
	Water	0% to 10%

Part II of the wash primer composition:

30	Phosphoric acid	10% to 25%
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Water	10% to 25%
Isopropyl alcohol	50% to 80%

(All percentages are by weight.)

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Examples of possible compositions are described in the following:

Example 1 A polyaniline wash primer formulation

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The wash primer consists of two parts, which are prepared according to the following formulation:

Part I Resin component

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An alcoholic solution was prepared by mixing 135 ml isopropyl alcohol, 45 ml n-butyl alcohol, and 5 ml water. 10.5 ml of polyaniline:poly(acrylic acid) 2% dispersion in water was added to the above-mentioned mixed alcoholic solution. The solution turned green in color. The solution was stirred for one hour. 17 gm of poly(vinyl butyral) resin (19% hydroxyl functionality) was slowly dissolved in the solution. The solution was continued to be stirred for 24 hours.

Part II Acid component.

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7.5 ml distilled water was added to 38 ml isopropyl alcohol. To this mixture, 5 ml of 85% phosphoric acid was added and stirred to form a solution.

Coating procedure:

Part I and Part II of the formulation were mixed immediately before coating. The mixture can be either brush painted or air sprayed onto freshly cleaned cold rolled steel or aluminum alloy (AA 6061) test coupons. The excess solution was allowed to drain off the sample. The coating thickness was measured to be about 0.4 mil.

5 After the green-colored coating was dried in the air, a commercial epoxy primer was applied on top of the wash primer. For example, a water-borne epoxy resin was applied by cathodic electrophoretic coating.

Example 2

10 Part I

A solution according to the method for part I of example 1 was prepared. It was slowly stirred. 16 gm of pigment grade molybdenum oxide, 2.4 gm magnesium silicate, and 0.2 gm
15 lamp black was added.

Part II is the same as Part II of example 1.

20 Example 3

The Polyaniline:poly(acrylic acid) complex in example 1 or example 2 may be replaced by one of the following complexes:

25 Polyaniline:Poly(vinylphosphate) complex.
Polyaniline:Poly(acrylic acid-co-vinylphosphate) complex.
Polyaniline:Poly(methacrylic acid-co-vinylphosphate) complex

30 Polypyrrole:Poly(vinylphosphate) complex.
Polypyrrole:Poly(acrylic acid-co-vinylphosphate) complex.
Polypyrrole:Poly(vinylmethacrylic acid-co-vinylphosphate) complex

Polyaniline:Poly(methylacrylate-co-vinylphosphate) complex
Polypyrrole:Poly(methylacrylate-co-vinylphosphate) complex

5 Polyaniline:Poly(butylacrylate-co-vinylphosphate) complex
Polypyrrole:Poly(butylacrylate-co-vinylphosphate) complex

10 II Electroactive surface pretreatment formulation

This part of invention is directed to the use of electroactive polymers as a component in a metal surface pretreatment formulation. This invention improves the performance of the 15 conventional iron phosphate and zinc phosphate pretreatment formulations.

Example 1

The following solution can be used for treating the surface of steel or aluminum alloys before coating with organic primer or topcoat. The range of the weight percentage of the 20 components is listed below.:

25	Polyaniline:poly(acrylic acid) complex	2% solid dispersed in water	1% to 20%
	Phosphoric acid (85% concentration)		30% to 80%
	Formic acid		0% to 10%
	Zinc oxide		0% to 6%
	Nitric acid		0% to 6%
	Water		20% to 60%

Example 2

This formulation replaces the polyaniline:poly(acrylic acid) complex by any one 30 or the combination of the following electroactive polymers:

Polyaniline:Poly(vinylphosphate) complex.

5 Polyaniline:Poly(acrylic acid-co-vinylphosphate) complex.
Polyaniline:Poly(methacrylic acid-co-vinylphosphate complex

5 Polypyrrole:Poly(vinylphosphate) complex.
10 Polypyrrole:Poly(acrylic acid-co-vinylphosphate) complex.
Polymer:Poly(vinylmethacrylic acid-co-vinylphosphate complex

10 Polyaniline:Poly(methylacrylate-co-vinylphosphate) complex
15 Polypyrrole:Poly(methylacrylate-co-vinylphosphate) complex
Polyaniline:Poly(butylacrylate-co-vinylphosphate) complex
Polymer:Poly(butylacrylate-co-vinylphosphate) complex

15 Example 3

This formulation includes the compositions defined in either example 1 or example 2 and the following additional compounds:

20 Ammonium fluoride 1% to 3%
Surfactant 0.5 to 1%

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III. A sealing formulation for commercial phosphate pretreatment process

Widely used commercial processes for metal surface pre-treatment include iron phosphating and zinc phosphating. During these processes, after the iron phosphate or zinc phosphate were applied to a metal surface, a chromate containing sealing solution was used to 25 apply a layer of hexavalent chromate. The function of the chromate is to inhibit corrosion. In this invention, a solution containing dispersible or soluble conducting polymer complex as a replacement of the chromate-based sealing wash is used.

30 Example 1

30 The formulation contains the following components:

Polyaniline:poly(acrylic acid) complex in water (0.5% to 10% by weight)

Example 2

The formulation contains the following components:

5 Polypyrrole:poly(acrylic acid) complex in water (0.5% to 10% solution)

Example 3

An alternative formulation includes:

10 Polyaniline:poly(methylacrylate-co-acrylic acid) complex in ethyl acetate. (0.5 % to 10 %)

Example 4

15 Polypyrrole:poly(methylacrylate-co-acrylic acid) complex in ethyl acetate. (0.5 % to 10 %)

Example 5

Using the same formulations as those in examples 1-4, except that the active ingredient is replaced by one of the followings:

20 Polyaniline:Poly(vinylphosphate) complex
Polyaniline:Poly(acrylic acid-co-vinylphosphate) complex
Polyaniline:Poly(methacrylic acid-co-vinylphosphate complex)

25 Polypyrrole:Poly(vinylphosphate) complex
Polypyrrole:Poly(acrylic acid-co-vinylphosphate) complex
Polypyrrole:Poly(vinylmethacrylic acid-co-vinylphosphate complex)

30 Polyaniline:Poly(methylacrylate-co-vinylphosphate) complex
Polypyrrole:Poly(methylacrylate-co-vinylphosphate) complex

IV. A coating system that allows non-destructive monitoring of corrosion activity under the coating.

In this invention, the electroactive component in the above-described wash primer or surface pretreatment coatings was used as an indicator for the extent or the rate of corrosion process at the metal-to-primer or metal-to-topcoat interfaces. Having a corrosion indicator under the paint allows the monitoring of the extent of corrosion usually hidden under the paint. This information is useful for preventive maintenance before catastrophic failure taking place. The knowledge may increase the safety of aircrafts, bridges and other structures depending on the mechanical strength of metals.

10 Additionally, the electroactive polymer were used as an indicator to signal the existence of corrosion under organic paint. The electroactive pretreatments on the metal surface contain electroactive polymers. These polymers can reversibly exchange electrons and protons with its immediate environment. For example, polyaniline has three forms with different degree of oxidation (by removing electrons from the polymer). The most reduced form is leuco emeraldine. By removing electrons from the polymer, the transparent leuco emeraldine transforms to the green colored emeraldine salt. When additional electrons were extracted, the green colored emeraldine salt transforms to the blue colored emeraldine base. With further oxidation, the blue colored emeraldine base is transformed into the purple colored pernigraniline. Protonation and deprotonation (extraction of proton) also causes transformation between the 15 green colored emeraldine salt and the blue colored emeraldine base. When the metal surface undergoes corrosion reactions, the electroactive polymer in the wash primer or the phosphate containing pretreatment will exchange electron or proton. If the primer and the topcoat are 20

transparent in the visible light spectrum, the color change of the pretreatment layer can be visualized and the change of color is indicative of the corrosion activity.

The visible color change may be masked if the paint has deep color. Although, this situation makes it harder for detecting the corrosion induced transformation of the conducting 5 polymer, it does not make the task impossible. In this case the transformation of the conducting polymer under the paint can be monitored by the difference in the optical absorption/reflection spectrum in the near infrared spectral region (wavelength in the range between 800 nm to 2500 nm). For most organic resins and pigments, the optical absorption spectrum in the near infrared region is weak, due to the overtone or combination band of vibrational spectrum of the organic 10 molecule. The electroactive polymers in its electrically conductive form have strong electronic absorption band (bands) in this spectral region. Thus, the paint covering the electroactive pretreatment is, to a large extent, transparent for the near infrared spectral range. When a near-infrared light is directed to the painted metal surface prepared with the electroactive formulation 15 described in this invention, the reflected light contain the information about the oxidation and protonation state of the conducting polymer (e.g., polyaniline). By using a microscopic near-infrared probe, one can obtain a spatially and spectrally resolved map of the oxidation and protonation states of the electroactive polymer in contact with the base metal. This information is helpful in locating the corrosion site. Information about the corrosion activity can be used to 20 assess whether preventive maintenance should be performed.

Since the early-warning indicator can be monitored optically without destruction of the organic coating, the process for monitoring corrosion can be scheduled at regular time intervals without damaging the coating. This saves time, money and the base material can monitored for deterioration.

V. An instrument for monitoring corrosion under paint without destruction of the paint.

1. An instrument for spot-checking without the capability of spatial resolution.

5 The invention is also directed to a hand held optical spectrometer that supplies light in the near infrared spectrum. The light can be focused on the surface of metal with electroactive pre-treatment or electroactive wash primer as the under-layer and the commercial paints as the over-layers. The light reflected from the surface is collected by an optical fiber wave-guide, and is sent to a spectrometer with diffraction grating and diode array detector. The electronic signal is
10 sent to a computer and the reflected spectrum is analyzed.

2. An instrument for spectrally resolved imaging of the electroactive polymer.

This instrument is a spectrally resolved digital camera. The camera has near-infrared sensitive two-dimensional array optical detectors.

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Although the present invention has been shown and described with respect to several preferred embodiments thereof, various changes, omissions and additions to the form and detail thereof, may be made therein, without departing from the spirit and scope of the invention.

20 What is claimed is: